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COMPLETE SPECIFICATION

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Photographic Silver Halide Films

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to heat-mouldable photographic films.

Heat-mouldable photographic films have been proposed which consist of a base of a cellulose derivative or synthetic resin and a silver halide emulsion layer, wherein a thermoplastic resin or cellulose derivative is used as the binding agent for the silver halide grains.

The present invention provides a heat-mouldable photographic film comprising a heat-mouldable base sheet, at least one anchoring sublayer and a light-sensitive layer comprising silver halide grains dispersed in a hydrophilic, macromolecular mixed polyvinyl acetal of a vinyl alcohol polymer which is water-soluble or hydrophilic in character, with benzaldehyde and an aldehyde substituted solely with a free carboxylic acid or a free sulphonic acid group or a water-soluble salt of such a substituted aldehyde. The light-sensitive layer may be coated with an anti-abrasion layer which may comprise a mixed polyvinyl acetal of a similar nature to that present in the light-sensitive layer.

The mixed acetals just described can be prepared by any conventional acetalisation process from (a) any vinyl alcohol polymer which is water-soluble or hydrophilic in character, including (1) polyvinyl alcohol of high molecular weight (viscosity of 4% aqueous solution at 20° C., 40 to 60 centipoises), (2) polyvinyl alcohol of medium molecular weight (viscosity of 4% aqueous solution at 20° C., 15 to 30 centipoises) which may be substituted with ester groups, e.g., acetate,

and propionate groups, and (3) 75—100% hydrolysed interpolymers of vinyl acetate with 0.05 to 0.5 mol. equivalents of terminally unsaturated mono-olefins, e.g., ethylene, as described in Specification No. 644,140, and (4) completely hydrolysed interpolymers of vinyl acetate with minor proportions (less than 50%) of polymerizable vinyl or vinylidene compounds, for example, vinyl chloride, vinyl cyanide or alkyl methacrylates, e.g. methyl or ethyl methacrylate, (b) benzaldehyde, and (c) an aldehyde substituted with a free carboxylic or sulphonic acid group or water-soluble salts of such a substituted aldehyde. For example, the acetalisation may be conveniently carried out in solution or suspension in water or an organic solvent or diluent using a catalyst such as phosphoric acid, sulphuric acid or hydrochloric acid. Suitable procedures and certain suitable aldehydes are described in Specification No. 535,341. The free acid groups can be converted into salt groups by a simple neutralisation.

The dimethyl or diethyl or ethylene glycol acetals of the aldehydes of compounds (b) and (c) can be used instead of the free aldehydes if desired; such an acetal interchange is described in Specification No. 535,341. An ethylene glycol reaction medium can also be used. Suitable hydrophilic, macromolecular acetals for practicing the invention are those having a vinyl alcohol content of 55 to 94%, a benzaldehyde content from 5 to 20%, and a substituted aldehyde content from 1 to 25%, percentages being by weight.

In a preferred aspect of the invention the polyvinyl acetals are made from polyvinyl alcohol or a polyvinyl ester which is at least 98% hydrolysed and contain *o*-sulphobenzaldehyde (preferably sodium *o*-sulphobenzaldehyde and benzaldehyde acetal groups and preferably have the constituent proportions mentioned in the preceding paragraph.

The heat-mouldable base sheet may conveniently comprise a copolymer of 100

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vinyl chloride and vinyl acetate predominating in the former and preferably containing 70—98% by weight in a copolymerised form. However other suitable heat-mouldable base material may be used. These include polystyrene, polyethylene, cellulose acetate, cellulose butyrate and non-oriented polyethylene terephthalate. Preferably the base contains an opacifier, e.g., titanium dioxide, zirconium dioxide or mixtures thereof.

In practicing the invention a heat-mouldable base sheet is provided with a suitable thin anchoring sublayer which is dried. An aqueous ethanol dispersion of light-sensitive silver halide in a mixed polyvinyl acetal described above is coated onto the sublayer and the resulting layer dried. These operations are, of course, carried out under conditions such that no substantial quantity of actinic light radiation, which would expose the silver halide, is present.

A suitable material for the anchoring sublayer comprises a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol predominating in the first of these components, and, optionally a compatible film-forming polymer, e.g., nitrocellulose, a hydrophilic, macromolecular polyvinyl acetal of *o*-sulphobenzaldehyde (or a water-soluble salt thereof) and, optionally, of benzaldehyde. This anchoring sublayer may be coated with one or two nitrocellulose layers.

The aqueous ethanol dispersions of light-sensitive silver halide in the hydrophilic, macromolecular mixed polyvinyl acetal can be prepared by precipitating the silver halide in an aqueous ethanol solution of said acetal by any conventional method of preparing silver halide dispersions in water-permeable colloids. Thus, a dilute aqueous ethanol solution of a soluble inorganic halide, e.g., ammonium bromide, potassium iodide or potassium chloride, or mixtures of any of these, can be admixed with the aqueous ethanol solution of said acetal and a dilute aqueous solution of a water-soluble silver salt, e.g., silver nitrate, sulphate, sulphamate, benzoate, acetate or citrate or a mixture of two or more of such salts. The two solutions can be added stepwise or simultaneously. After the solutions are mixed and the silver halide dispersion formed, the mixture is allowed to ripen at ordinary or moderately elevated temperatures e.g., 25 to 50° C., until the silver halide grains acquire the desired grain size.

In one form of the invention the mouldable film consists of a sheet of a copolymer of vinyl chloride and vinyl acetate containing 70 to 98% by weight of copolymerised vinyl chloride, said sheet bear-

ing in order a single sublayer comprising a polymer of vinyl chloride, vinyl acetate and vinyl alcohol and a compatible film-forming polymer, e.g., nitrocellulose; a hydrophilic, macromolecular mixed benzaldehyde/*o*-sulphonbenzaldehyde polyvinyl acetal of the type described above, or a polyvinyl acetal containing carboxylic or sulphonic acid groups, or their water-soluble salts described in Specification No. 600,039, a layer of a light-sensitive silver halide in the hydrophilic, macromolecular mixed benzaldehyde/-substituted aldehyde polyvinyl acetal described above and if desired an antiabrasion layer which may be composed of one of the polyvinyl acetals described in this paragraph. The above layers can be applied by the conventional coating methods.

Another suitable heat-mouldable film according to the invention has a base sheet of the composition given in the preceding paragraph, bearing in order a sublayer comprising 3 parts of terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol and 1 part of nitrocellulose, a sublayer comprising a hydrophilic, macromolecular mixed benzaldehyde/*o*-sulphobenzaldehyde polyvinyl acetal of the type described above, and a layer of light-sensitive silver halide as described in the preceding paragraph and, if desired, an antiabrasion layer composed of one of the aforesaid mixed polyvinyl acetals. The above layers can be applied by conventional coating methods.

In applying the light-sensitive polyvinyl acetal layer it is convenient to use a water-soluble boron compound capable of yielding borate ions, e.g., boric acid, as described in Specification No. 641,368, since it causes rapid gelling of the light-sensitive layer. The boron compound can be included as a component of the sublayer on which the light-sensitive silver halide layer is coated.

In using the film, for instance in making a contour map, the heat-mouldable film is first moulded under heat, then exposed to photographic negative pictures of terrain, and developed, washed and fixed in the same manner as a photographic paper print.

The invention is illustrated by the following examples. The percentages stated are by weight, unless otherwise indicated, and the processes are carried out in the substantial absence of actinic light rays.

EXAMPLE I

A film base sheet, approximately 10 mils in thickness, of a copolymer of vinyl chloride and vinyl acetate (87:13 by weight respectively) which contained

- sufficient white pigment to render it light-opaque was provided with a thin anchoring sublayer by coating its surface from a solution made by admixing the following components:—
- 5 Mixed benzaldehyde (7 parts) sodium *o*-sulphobenzaldehyde (13 parts) polyvinyl acetal of polyvinyl alcohol (100 parts) (medium viscosity) - - - 1.5%
 10 Ethanol (95%) - - - 26.57%
 Acetone - - - 69.08%
 Boric acid - - - 1.89%
- 15 Terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol (91:3:6 by weight respectively) - - - 0.96%
- 20 The sublayer was dried and an aqueous ethanol dispersion of silver bromide in a mixed sodium *o*-sulphobenzaldehyde/benzaldehyde acetal made by reacting 100 parts of polyvinyl alcohol (medium viscosity) with 7 parts of the former and 13 parts of the latter aldehyde was coated onto the sublayer and dried. There was then coated on the emulsion layer a thin anti-abrasion layer from an aqueous ethanol solution of the same mixed acetal.
- 30 The resulting heat-mouldable film, after drying, was placed emulsion side down over a plaster of Paris mould conforming to the contour of an area of terrain, said mould having a plurality of spaced vertical air-reduction holes and being disposed in a heat-moulding apparatus of the type described in United States Patent No. 2,493,439. The said apparatus comprises a vacuum box with an open side adapted to accept the mould, a hooded reflection and hot air heating means overlying the open face of the box.
- 45 The apparatus was provided with a vacuum pump or aspirator to remove air between the film and the mould. A heat source at approximately 700° F. was placed in close proximity to the film for 5 to 15 seconds and a vacuum of about 28 inches of mercury applied beneath the mould for one second. The heat source was then removed. After cooling, the moulded film was removed and placed on a photographic enlarging table where a negative photographic picture containing objects on the surface of the original terrain was projected in register with the contour of the moulded film thereby exposing the light-sensitive surface of the formed photographic film. The exposure was about 10 to 15 seconds at f 16 with a 1.3 times magnification. After exposure, the shaped exposed photographic film was processed as follows:—
- (1) developed for five minutes at 70° F. in a solution made by admixing the following components:—
- Water - - - 750.0 cc.
 N-methyl-*p*-aminophenol hydro-sulphate - - - 3.0 gms.
 Sodium sulphite (anhydrous) - - - 45.0 gms.
 Hydroquinone - - - 12.0 gms.
 Sodium carbonate monohydrate - - - 79.0 gms.
 Potassium bromide - - - 1.9 gms.
 Water to make - - - 1 litre
- (2) rinsed in water at 65° F. for 30 seconds,
- (3) fixed for seven minutes at 68° F. in a solution made by admixing the following components:—
- Sodium thiosulphate crystals - - - 240.0 gms.
 sodium sulphite (anhydrous) - - - 15.0 gms.
 Borax - - - 18.0 gms.
 Glacial acetic acid - - - 12.0 cc.
 Potassium alum - - - 20.0 gms.
 Water to make - - - 1 litre
- (4) washed in water at 65° F. for 10 minutes and dried.
- The heat-mouldable film of this example had good moulding characteristics and there was excellent adherence between all layers during and after the heat-moulding and photographic processing steps. The relief photograph of terrain was free from blisters and no cracking, buckling or "creasing" occurred during or after the moulding operation.
- ### EXAMPLE II
- A film base as described in Example I was provided with a thin anchoring sublayer by coating its surface from a solution made by admixing the following components:—
- Terpolymer as in Example I 3.0%
 Nitrocellulose (nitrogen content 11.75%—11.99%) - - - 1.0%
 Acetone to 1000 ml. - - - 96.0%
- The layer was dried and a thin sublayer was applied to it from a solution containing 1.5% of a mixed sodium *o*-sulphobenzaldehyde/benzaldehyde acetal made by reacting 100 parts by weight of polyvinyl alcohol (medium viscosity) with 7 parts of the former and 13 parts of the latter aldehyde. The resulting layer was dried and a light-sensitive emulsion layer was applied from an aqueous ethanol dispersion of silver bromide in a further portion of the same mixed acetal. There was then coated on the emulsion layer a thin anti-abrasion layer from an aqueous ethanol solution of the same mixed acetal. The resulting film after drying was converted into a moulded

photograph in the same manner as described in Example I and it had similar characteristics.

EXAMPLE III

5 A film base as described in Example I was provided with a thin anchoring sublayer by coating its surface with a solution made by admixing the following components:—

- 0 Terpolymer as in Example I 10%
Acetone - - - - - 90%

On the sublayer there was then coated a thin nitrocellulose layer from a solution of nitrocellulose (nitrogen content 11.75% to 11.99%) in acetone. The layer was dried and a thin sublayer was applied to it from an aqueous solution containing 1.5% of a mixed *o*-sulphobenzaldehyde/benzaldehyde polyvinyl acetal made by reacting 100 parts by weight of polyvinyl alcohol (medium viscosity) with 7 parts of the former and 13 parts of the latter aldehyde. A light-sensitive silver halide emulsion layer was then applied from an aqueous ethanol dispersion of silver bromide in a further portion of the same mixed acetal. There was then coated on the emulsion layer a thin anti-abrasion layer from an aqueous ethanol solution of the same mixed acetal. The resulting film, after drying, was converted into a moulded photograph in the same manner as described in Example I with similar characteristics.

35 Additional heat-mouldable photographic films of the type described in Examples I, II and III are made by substituting for the mixed benzaldehyde sodium *o*-sulphobenzaldehyde polyvinyl acetals used in the sublayers, light-sensitive emulsion layers, and anti-abrasion layers in the films of such examples, mixed polyvinyl acetals containing the following proportions of components:—

- 45 (1) 100 parts of polyvinyl alcohol acetalised by reaction with 4 parts sodium *o*-sulphobenzaldehyde and 13 parts benzaldehyde.
50 (2) 100 parts of polyvinyl alcohol acetalised by reaction with 14 parts sodium *o*-sulphobenzaldehyde and 13 parts benzaldehyde.
55 (3) 100 parts of polyvinyl alcohol acetalised by reaction with 22 parts sodium *o*-sulphobenzaldehyde and 13 parts benzaldehyde.
60 (4) 100 parts of polyvinyl alcohol acetalised by reaction with 2 parts sodium *o*-sulphobenzaldehyde and 8.5 parts benzaldehyde.

These films, when processed in like manner, had similar properties.

While the above examples are all directed to the use of the preferred mixed benzaldehyde/sodium *o*-sulphobenzaldehyde

hyde acetals similar films can be made by substituting for the sodium *o*-sulphobenzaldehyde like proportions of other aromatic or aliphatic aldehydes substituted with free carboxylic or sulphonic acid groups or water-soluble salts thereof such as phthalaldehyde acid and propionaldehyde- β -sulphonic acid as described in Specification No. 535,341. These acetals and particularly those made from *o*-sulphobenzaldehyde, have excellent water-permeable characteristics and readily absorb developing solutions so that good photographic silver images can be made. The layers have extraordinary resistance to chemical fog which is induced by heat. These desirable characteristics are not possessed by polyvinyl acetals made solely from aliphatic aldehyde, aromatic aldehydes or mixed aliphatic-aromatic aldehydes free from solubilizing groups.

The silver halide emulsion may contain various adjuvants including sensitising dyes, fog inhibitors, e.g., benzotriazole, 5-mercaptotetrazoles, 5-mercapto-1:3:4-triazoles, 1-phenyl-5-mercaptotetrazoles, wetting agents of the anionic, cationic and non-ionic type including sodium alkyl sulphates and sulphonates and C- and N-alkylbetaines wherein the alkyl groups contain 8 to 18 carbon atoms.

The particular combination of benzaldehyde and *o*-sulphobenzaldehyde acetal groups, has exceptionally useful properties and the novel relationship of layers described above provides a heat-mouldable film having photographic characteristics comparable with the best commercial photographic papers.

The base sheet used in accordance with the invention should mould readily to conform to an irregular surface like that in a relief map of rugged terrain at temperatures between 150 and 300° F. and retain their structural strength after the moulding operation.

The heat-mouldable films of this invention can be used for various purposes where a photographic image or picture is desired on an irregular surface. Thus, it can be used for various decorative purposes, e.g., wall plaques and lamp shades. It is especially useful in the preparation of relief maps for military and other purposes. They can be heat moulded at temperatures as high as 300° F. without impairing the excellent adherence between the base and coated layers or their photographic properties.

The heat-mouldable films of this invention may be exposed, processed and then moulded, or in an alternative procedure, may be exposed, moulded and then processed without impairing the excellent adhesion between the base and coated

layers, or the fidelity of the moulding qualities, or the photographic properties of the films.

- The mouldable films of this invention, therefore, have a number of important and valuable properties. In particular, the photographic quality is not seriously affected deleteriously by the heat-moulding operation, e.g., the operation does not cause any substantial fogging or staining or seriously disturb the uniformity of the silver halide dispersion and the light-sensitive layer has excellent permeability to the developing, washing, and fixing solutions after the heat-moulding operation. Moreover, the films are of good photographic speed and contrast and may be used to make photographic relief maps in a rapid manner and conforming to the original mould.

What we claim is:—

1. A heat-mouldable photographic film comprising a heat-mouldable base sheet, at least one anchoring sublayer and a light-sensitive layer comprising silver halide grains dispersed in a hydrophilic, macromolecular mixed polyvinyl acetal of a vinyl alcohol polymer which is water-soluble or hydrophilic in character, with benzaldehyde and an aldehyde substituted solely with a free carboxylic acid or a free sulphonic acid group or a water-soluble salt of such a substituted aldehyde.
2. A heat-mouldable film as claimed in Claim 1 in which said light-sensitive layer is coated with an anti-abrasion layer.
3. A heat-mouldable film as claimed in Claim 2 in which said anti-abrasion layer comprises a mixed polyvinyl acetal of a similar chemical composition to that present in the light-sensitive layer.
4. A heat-mouldable film as claimed in any of the preceding claims in which said base sheet contains an opacifier.
5. A heat-mouldable film as claimed in any of the preceding claims in which said base sheet comprises a copolymer of vinyl chloride and vinyl acetate predominating in the former.
6. A heat-mouldable film as claimed in Claim 5 in which said copolymer contains 70—98% by weight of copolymerised vinyl chloride.
7. A heat-mouldable film as claimed in any of the preceding claims in which said anchoring sublayer comprises a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol predominating in the first of these.
8. A heat-mouldable film as claimed in Claim 7 in which said anchoring sublayer further contains or is supercoated with nitrocellulose.
9. A heat-mouldable film as claimed in Claim 7 in which said anchoring sublayer further contains or is supercoated with a hydrophilic, macromolecular polyvinyl acetal of *o*-sulpho-benzaldehyde (or a water-soluble salt thereof) and of benzaldehyde.
10. A heat-mouldable film as claimed in any of the preceding claims in which said mixed polyvinyl acetal of said light-sensitive layer has a polyvinyl alcohol content of 55—94%, a benzaldehyde content of 5—20% and a substituted aldehyde content of 1—25%, percentages being by weight.
11. A heat-mouldable film as claimed in any of the preceding claims in which the substituted aldehyde in the mixed polyvinyl acetal of the light-sensitive layer is *o*-sulpho-benzaldehyde or a water-soluble salt thereof.
12. A heat-mouldable film as claimed in Claim 11 in which said substituted aldehyde is sodium *o*-sulpho-benzaldehyde.
13. A heat-mouldable photographic film as claimed in any of the preceding claims with particular reference to any one of the foregoing Examples Nos. I to III.
14. A process of preparing a heat-mouldable film as claimed in any of the foregoing claims in which a heat-mouldable base sheet is coated with, in order, at least one anchoring layer and a light-sensitive layer comprising silver halide grains dispersed in a hydrophilic, macromolecular mixed polyvinyl acetal of a vinyl alcohol polymer which is water-soluble or hydrophilic in character with benzaldehyde and an aldehyde substituted solely with a free carboxylic acid or a free sulphonic acid group or a water-soluble salt of such a substituted aldehyde.
15. A process as claimed in Claim 14 in which the said light sensitive layer is coated in the presence of a water-soluble boron compound capable of yielding borate ions.
16. A moulded and processed photographic film manufactured from a heat-mouldable film claimed in any Claim from 1 to 13.

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